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# ENGINEERING DATA TRANSMITTAL

Page 1 of 1

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**This document was reviewed following the procedures described in WHC-CM-3-4 and is:**

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6. Author

Name: B. C. CARPENTER

Bcarpenter
Signature

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7. Abstract

This document is a plan which serves as the contractual agreement between the Characterization Program, Sampling Operations, WHC 222-S Laboratory, Oak Ridge National Laboratory, and PNL 329 Laboratory. The scope of this plan is to provide guidance for the sampling and analysis of vapor samples from tank 241-BY-103.

8. RELEASE STAMP

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DATE OCT 21 1994
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WHC-SD-WM-TP-231
Revision 0

# Tank 241-BY-103
# Tank Characterization Plan

Prepared for the U.S. Department of Energy
Office of Environmental Restoration
and Waste Management

SAMPLE EVENT A: VAPOR SAMPLING IN FISCAL YEAR 1995

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## LIST OF FIGURES



## LIST OF ACRONYMS

| | |
|---|---|
| BY-103 | Tank 241-BY-103 |
| CERCLA | Comprehensive Environmental Response, Compensation, and Liability Act of 1980 |
| CGM | combustible gas meter |
| DOT | Department of Transportation |
| DQO | data quality objective |
| ECN | engineering change notice |
| EPA | Environmental Protection Agency |
| ESH&QA | Environmental Safety, Health, and Quality Assurance |
| FAS | Field Analytical Services |
| GC/MS | gas chromatography/mass spectrometry |
| IC | ion chromatography |
| IDLH | imediately dangerous to life and health |
| ISS | in-situ sampling |
| LFL | lower flammability limit |
| OGIST | Oregon Graduate Institute of Science and Technology |
| ORNL | Oak Ridge National Laboratory |
| PNL | Pacific Northwest Laboratory |
| ppbv | parts per billion by volume |
| ppmv | parts per million by volume |
| RCRA | Resource Conservation and Recovery Act |
| SACS | Surveillance Analysis Computer System |
| SML | Sampling and Mobile Laboratories |
| SUMMA® | registered trademark for passivated stainless steel canister |
| TCP | Tank Characterization Plan |
| TNMHC | Total Non-Methane Hydrocarbons |
| TRP | Toxicology Review Panel |
| TO-12 | EPA task order protocol 12 |
| TO-14 | EPA task order protocol 14 |
| TOC | total organic carbon |
| TWRS | Tank Waste Remediation System |
| VSS | vapor sampling system |
| WHC | Westinghouse Hanford Company |

# TANK 241-BY-103 VAPOR SPACE TANK CHARACTERIZATION PLAN

## 1.0 SPECIFIC TANK VAPOR SPACE CHARACTERIZATION OBJECTIVES

The sampling and analytical needs associated with the 51 Hanford Site underground storage tanks classified on one or more of the four Watch Lists (ferrocyanide, organic, flammable gas, and high heat), and the safety screening of all tanks have been identified through the Data Quality Objective (DQO) process. Sampling of the vapor space will identify: 1) volatile compounds above the surface of the waste; and 2) the amount of gases generated by chemical or radiolytic reactions within the waste.

This Tank Characterization Plan will identify vapor space characterization objectives for tank BY-103 pertaining to sample collection, sample preparation and analysis, and laboratory analytical evaluation and reporting requirements in accordance with the *Tank Waste Remediation System Tank Waste Analysis Plan* (Haller 1994) and the applicable Data Quality Objectives identified in the following sections. In addition, an estimate of the current contents and status of the tank is given.

### 1.1 Tank Vapor Space Safety Screening Data Quality Objectives

The *Tank Safety Screening Data Quality Objective* (Redus and Babad 1994) describes the sampling and analytical requirements that are used to screen waste tanks for unidentified safety issues. Both Watch List and non-Watch List tanks will be sampled and evaluated to identify tank vapor space safety conditions related to the ferrocyanide, organic, and flammable gas safety issues. Each of these issues requires that each tank be screened to determine the flammability of gases in the vapor space of the tank.

### 1.2 Health and Safety Vapor Issue Resolution Data Quality Objectives

The *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Issue Resolution* (Osborne et al. 1994a) concerns the tanks on the current "Suspect Tank List" and describes the methodology used to: 1) identify those tanks which can safely be sampled with intrusive equipment without risk of gas ignition; and 2) identify and estimate concentrations of toxicologically significant compounds present in the tank headspace and compare to published (if available) exposure limits.

### 1.3 Vapor Sampling Data Quality Objectives to Support Rotary Core Sampling

A portable modular exhauster has been developed to exhaust the tank atmosphere during a rotary drill sampling operation. Characterization of the tank headspace is needed to support exhauster start-up and define operational monitoring parameters. The *Rotary Sampling Core Vapor Sampling Data Quality Objective* (Price et al. 1994) defines requirements needed to identify the potential for release of regulated pollutants, confirm that the exhauster can be safely started, and establish alarm setpoints for total organic carbon (TOC) and ammonia release to maintain safe exhauster operation. To start the exhauster, the flammability and concentration of toxic gases in the tank vapor space is needed.

### 1.4 Ferrocyanide Tank Safety Issues Data Quality Objectives

The *Data Requirements for the Ferrocyanide Safety Issue Developed through the Data Quality Objective Process* (Meacham et al. 1994) identifies the requirements needed to identify a ferrocyanide Watch List tank as SAFE, CONDITIONALLY SAFE, or UNSAFE. Since ferrocyanide is non-volatile, only gaseous reaction products such as nitrogen compounds may be present in the vapor space. Although this DQO does not specify vapor measurements, the vapor data will be used to corroborate data obtained from past and/or future tank core analyses.

## 2.0 RELEVANT SAFETY INFORMATION

Potential fugitive vapor emissions from the tanks could become worker health and safety issues.

### 2.1 Tank Status

Single-shell tank BY-103 is classified as a Ferrocyanide Watch List tank and was declared an assumed leaker in 1973.

Tank BY-103 is estimated to contain 34,000 liters (9,000 gal.) of sludge and 1,480,000 liters (391,000 gal.) of saltcake for a total of 400,000 gal. The saltcake is estimated to contain 520,000 liters (137,000 gal) of pumpable interstitial liquid. Its contents are categorized as non-complexed waste (NCPLX) (Hanlon 1994). The median temperature of the waste in tank BY-103 is 24.9°C; the maximum temperature is 58.3°C.

Recent readings (July, 1994) obtained from Tank Farm Surveillance and the Surveillance Analysis Computer System (SACS) database indicate a waste depth of 147.5 inches below riser 5, which is located on the easth side approximately 1/4 of the radius from the center of the tank. From this, the total waste volume is calculated at 1,580,000 liters (418,000 gal.).

### 2.2 Tank Monitoring Activities

Waste level measurements are taken through riser 4 using a manual tape. Internal tank temperature is automatically recorded from 15 thermocouples on a tree in riser 1. A liquid observation well is located in riser 7. Six active dry wells monitor radiation in the surrounding soil (Brevick et al. 1994).

## 3.0 SUMMARY OF HISTORICAL INFORMATION FOR TANK BY-103

Included in this section are a physical description of tank BY-103, its process history, and recorded sampling events.

### 3.1 Configuration

Tank BY-103 is one of 16 single-shell tanks in the 200 East area BY Farm constructed during 1948-49. It is 23 meters (75 ft.) in diameter with a concave-shaped base and has a 2.87 million liter (758 Kgal) tank capacity. The tank was the last one in a three tank cascade series. The first two tanks were BY-101 and BY-102.

### 3.2 Process History

Tank BY-103 received metal waste from tank BY-102 from October 1950 to March 1952. Tanks contents were transferred to tanks C-104, C-105, and BY-109 in 1954 and was used as a TBP scavenged waste receiver until 1965. From 1965 until 1972 the tank received CW waste and was for ITS bottoms and recycle. The tank was declared an assumed leaker in 1973 with a leak volume greater than 5000 gal. A saltwell was installed and primary stabilization completed in 1977. Level adjustments were made in 1980 and 1982 and partial isolation completed in 1982. A major level adjustment was made in September 1987 by jet pumping and the last level adjustment completed in April 1990. (see Figure 1).

### 3.3 Historical Sampling Events

Tank BY-103 supernatant was sampled in 1990 and analyzed in 1991 for a limited set of physical and chemical analytes. Table 1 lists the laboratory analysis results for this sample.

A type 2 vapor insitu sampling (ISS) event collected vapor space samples from tank BY-103 on May 5, 1994. Three SUMMA® canister samples were collected from the tank headspace and shipped to the Oregon Graduate Institute of Science and Technology for analysis following Letter of Instruction guidelines (Osborne 1994b). Modified EPA TO-12 and TO-14 methods were applied to analyze the organic vapor. Analyses for nitrous oxide, hydrogen, and carbon monoxide were also performed. A data letter report, submitted to the TWRS Tank Vapor Issue Resolution Program, was produced as screening data and is not qualified data. These results and 9 of the 42 EPA TO-14 compounds detected are given in Table 2.

Results of an ambient air SUMMA® canister sample (field blank) collected upwind of BY-103 for volatile organics following procedure EPA TO-12 were not reported. Nitrous oxide was found at 0.8 ppmv. Hydrogen and carbon monoxide were not detected.

Table 1. Historical Characterization Data For Tank BY-103.

| SAMPLE | R8088 |
|---|---|
| DATE | 6/3/91 |
| RADIONUCLIDES | |
| Total Alpha µCi/L | 0.68 |
| Total Beta µCi/L | 365,100 |
| GEA-liq µCi/L | 200,00 Cs-137 |
| Sr-89/90 µCi/L | 233 |
| Tc-99 µCi/L | 117 |
| Pu-239/40 µCi/L | < |
| Am-241 µCi/L | < |
| CHEMICAL COMPONENTS* | |
| Na ppm | 199,000 |
| Al ppm | 38,400 |
| K ppm | 5,900 |
| Cr ppm | 543 |
| Pb ppm | 151 |
| Fe ppm | 82 |
| Si ppm | 55 |
| Mo ppm | 53 |
| Sn ppm | 48 |
| Bi ppm | 15 |
| Ca ppm | 3 |
| Mg ppm | 3 |
| Cd ppm | 2 |
| Mn ppm | 1 |
| Sr ppm | 1 |
| Ba ppm | 1 |
| As mg/L | 1.8 |
| Se mg/L | 7.6 |
| Hg ppm | < |
| OH M | 2.6 |
| NO2 ppm | 63,000 |
| NO3 ppm | 190,000 |
| CO3 M | 0.34 |
| PO4 ppm | <2,100 |
| SO4 ppm | 7,200 |
| TOC (g/L C) | 2.7 |
| PHYSICAL DATA | |
| Sp. Gr. | 1.45 |
| % Water | 52 |

< Less than detection limit.

Table 2. Vapor Space Characterization Data for Tank BY-103.

| Compound | Sample Identification Numbers | | |
|---|---|---|---|
| | 106 | 107 | 108 |
| TNMHC[1] by procedure TO-12, $\mu g/m^3$ | 5,190 (± 14) | 4,764 (± 60) | 5,513 (± 5) |
| Nitrous Oxide, ppmv | 49.2 | 49.2 | 49.2 |
| Hydrogen, ppmv | 21.8 | 21.2 | 21.2 |
| Carbon Monoxide, ppmv | < 1 | < 1 | < 1 |
| Non-Methane VOC by procedure EPA TO-14, ppbv | | | |
| Freon 12 | 1 | 1 | 1 |
| Methylchloride | 1 | 1 | 1 |
| 1,3-Butadiene | 2 | 1 | -- |
| Freon 11 | 95 | 67 | 60 |
| Benzene | 2 | 1 | 1 |
| Toluene | 33 | 25 | 23 |
| Perchloroethylene | 1 | 1 | 1 |
| m&p-Xylene | 1 | 1 | 1 |
| o-Xylene | 1 | 1 | -- |

[1]Total Non-Methane Hydrocarbons

### 3.3.1 Expected Tank Dome Space Vapor Composition

The quantification of the total non-methane hydrocarbons by the EPA TO-12 procedure indicates a low level of organic vapors in the tank BY-103 vapor space. Other vapors of concern which may be present in the vapor space are ammonia, methane, nitric oxide, and nitrogen dioxide.

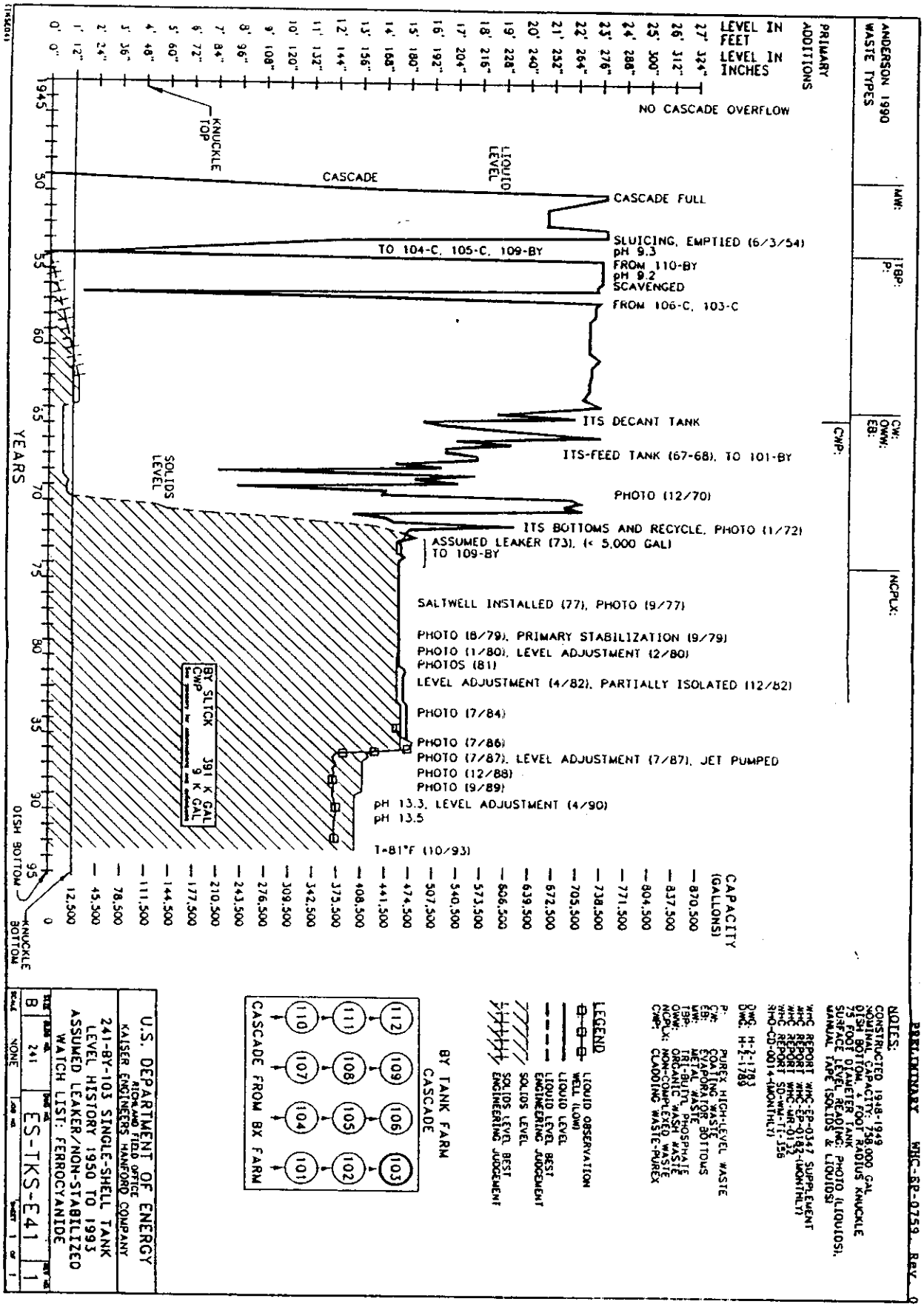



Figure 1. Fill history of Tank 241-BY-103.



U.S. DEPARTMENT OF ENERGY
RICHLAND FIELD OFFICE
KAISER ENGINEERS HANFORD COMPANY

241-BY-103 SINGLE-SHELL TANK
LEVEL HISTORY 1950 TO 1993
ASSUMED LEAKER/NON-STABILIZED
WATCH LIST: FERROCYANIDE

B | 241 | ES-TKS-E41 | 1

NONE

# 4.0 SCHEDULED SAMPLING EVENT

The following information provides the methodology and procedures to be used in the preparation, sample retrieval, transport, analysis, and reporting of results for vapor space samples retrieved from tank BY-103. Any decisions, observations, or deviations to this characterization plan made during sample receipt, preparation, and analysis shall be documented in the deliverable report.

## 4.1 Preparation of Sample Media Containers

The laboratory performing the contracted analytical work shall supply prepared and labeled sample containers (SUMMA® canisters and/or selective sorbent sampling media) to Field Analytical Services (FAS) at least 48 hours in advance of the scheduled sampling date. Each sample media container is certified that preparation procedures were performed and it complies to cleanliness requirements. FAS shall provide sample identification numbers following the quality assurance/quality control format given in Section 5.1 and other label information to the laboratories as requested.

## 4.2 Flammability of Vapor Space Gases

Prior to performing intrusive work on a tank, an assessment of the flammability of the tank vapor space gases is required by standard WHC safety practices. Under present guidelines no operational or sampling activity is permitted if a single sample of the tank vapor fuel content, as measured with a combustible gas meter (CGM), is greater than 20% of the lower flammability limit (LFL). If this CGM sample has a total fuel content between 10% and 20% of the LFL, a vapor sampling activity may continue under CGM monitoring to better identify the hazard level. Under 10% of the LFL the tank is not considered a flammability problem and all scheduled work can proceed (Osborne et al. 1994a).

## 4.3 Sample Collection

In fiscal year 1995, the tank BY-103 vapor space shall be sampled through a heated probe in riser 10B using the vapor sampling system (VSS) in accordance with laboratory operating procedure LO-080-450 "Collection of SUMMA® Canisters & Sorbent Tube Samples Using the Vapor Sampling System (VSS)". Table 3 specifies the sample type, the type of collection media to be used, and the number of samples requested. Table 4 provides a sequence of sampling activities and specifies the sample collection time and the flow rate through the sample collection tubes.

A cleanliness check shall be performed in accordance with procedure LO-080-450, Appendix C. Cleanliness of the VSS shall also be addressed by collecting ambient air SUMMA® samples prior to sampling the tanks using the following conditions: 1) with the VSS manifold and transfer lines fully heated; and 2) without the VSS, upwind of BY-103.

The GC/FID shall be used to monitor organic vapors during the sampling event. The GC/FID shall be operated in accordance with LO-080-450, Appendix D and Bellus (1993).

Table 3. General Sampling Information

| Sample Container | Prepared By | Preparation Procedure | Sample Type | Number of Samples |
|---|---|---|---|---|
| SUMMA® | PNL | PNL-TVP-002 | Tank Air | 6 |
| SUMMA® | PNL | PNL-TVP-002 | Ambient Air[2] | 2 |
| Triple Sorbent Traps | ORNL | AC-OP-300-0907 CASD-AM-300-WP01[3] | Tank Air | 4 |
| | ORNL | AC-OP-300-0907 | Field Blank | 1 |
| | ORNL | AC-OP-300-0907 | Trip Blank | 1 |
| Sorbent Trap System for $NH_3$, $NO_2$, NO, $H_2O$ | PNL | PNL-TVP-002 | Tank Air | 6 |
| | PNL | PNL-TVP-002 | Trip Blank | 3 |
| Tritium Trap | WHC | LA-548-111 | Tank Air | 1 |
| HEPA Filters | WHC | N/A | Tank Air | 4 |

[2]One sample taken through the VSS, one sample taken upwind of the tank.
[3]Preparation procedure for samples spiked with surrogate(s).

## 4.4 Radiation Screening and Sample Transport

All samples shall be stored at the 222-S Laboratory Annex following The sample receipt and control procedure PNL-TVP-07 while performing a radiological survey of the HEPA filters used in the VSS and the tritium trap sampler. This is necessary to comply with Department of Transportation (DOT) shipping regulations and offsite laboratory acceptance criteria.

The HEPA filters used in the VSS shall be received by the 222-S Laboratory and analyzed for the acceptable specific (alpha, beta, gamma) activity levels given in Table 5. The Tritium Trap shall be analyzed at the 222-S Laboratory for tritium using liquid scintillation counting to determine tritium activity.

The results from the radiation screening shall be submitted to and evaluated by Field Analytical Services to ensure the samples meet the analytical laboratory's acceptance criteria. Field Analytical Services shall provide a report to each analytical laboratory to identify the number of picocuries per sample (pCi/g of sample) for each sample that is submitted for analysis.

Table 4. List of Samples and Activities.

| SAMPLE CODE | SAMPLE/ACTIVITY DESCRIPTION | SAMPLER POSITION DURING COLLECTION | GAS FLOW RATE | SAMPLE DURATION |
|---|---|---|---|---|
| | | | | |
| -- | Purge VSS with ambient air[4] | N/A | 5,450 mL/min | 30 min. |
| 01 | Collect ambient air sample SUMMA #1 | Upwind of BY-103 | | 1 min. |
| -- | Collect GC sample and initiate GC run | | | |
| 02 | Collect ambient air sample SUMMA #2 | Port 15 | | 1 min. |
| -- | Leak test | N/A | | |
| -- | Purge VSS with tank air | N/A | 5,450 mL/min | 30 min. |
| -- | Measure tank pressure | N/A | N/A | N/A |
| 03 | Collect Tritium Trap | Sorbent line 8 | 200 mL/min | 5 min. |
| -- | Collect GC sample and initiate GC run | | | |
| 04 | Collect SUMMA #3 | Port 11 | | 1 min. |
| 05 | Collect SUMMA #4 | Port 13 | | 1 min. |
| 06 | Collect SUMMA #5 | Port 15 | | 1 min. |
| 07 | Collect SUMMA #6 | Port 12 | | 1 min. |
| 08 | Collect SUMMA #7 | Port 14 | | 1 min. |
| 09 | Collect SUMMA #8 | Port 16 | | 1 min. |
| 10 | Collect Triple Sorbent Trap (TST) sample #1 | Sorbent line 9 | 200 mL/min | 5 min. |
| 11 | Collect TST sample #2 | Sorbent line 10 | 200 mL/min | 5 min. |
| 12 | Open, close, & store TST Field Blank #1 | In VSS truck | 0 mL/min | |
| 13 | Collect TST sample #3 | Sorbent line 8 | 200 mL/min | 5 min. |
| 14 | Collect TST sample #4 | Sorbent line 10 | 200 mL/min | 5 min. |
| 15 | Store TST Trip Blank #1 | None | None | None |
| 16 | Collect NH3/NOx/H2O Sorbent Trap #1 | Sorbent line 9 | 200 mL/min | 15 min. |
| 17 | Collect NH3/NOx/H2O Sorbent Trap #2 | Sorbent line 10 | 200 mL/min | 15 min. |
| 18 | Collect NH3/NOx/H2O Sorbent Trap #3 | Sorbent line 8 | 200 mL/min | 15 min. |
| 19 | Collect NH3/NOx/H2O Sorbent Trap #4 | Sorbent line 10 | 200 mL/min | 15 min. |
| 20 | Collect NH3/NOx/H2O Sorbent Trap #5 | Sorbent line 9 | 200 mL/min | 15 min. |
| 21 | Collect NH3/NOx/H2O Sorbent Trap #6 | Sorbent line 10 | 200 mL/min | 15 min. |
| 22, 23, 24 | Store NH3/NOx/H2O Trap Trip Blanks #1, #2, & #3 | None | None | None |
| 25 | Remove upstream HEPA Filter from HEPA transfer box | Upstream of box | Continuous | |
| 26 | Remove downstream HEPA Filter from HEPA transfer box | Downstream of box | Continuous | |
| 27 | Remove upstream HEPA Filter from VSS | Upstream of VSS | Continuous | |
| 28 | Remove downstream HEPA Filter from VSS | Downstream of VSS | Continuous | |

[4]Not required if ambient air purge incorporated in VSS setup.

Table 5. Limits For Acceptable Radionuclide Activity Levels.

| Organization | Total $\alpha$ | Total $\beta/\gamma$ | Tritium | Units |
|---|---|---|---|---|
| PNL Analytical Chemistry Laboratory | $\leq$ 100 | $\leq$ 400 | -- | pCi/g |
| Oak Ridge National Laboratory | $\leq$ 135 | $\leq$ 450 | -- | pCi/g |
| WHC-CM-2-14[5] | $\leq$ 60 | $\leq$ 200 | -- | pCi/g |

[5] Samples above DOT limits may be shipped as Limited Quantity of Radioactive Material in accordance with DOT approval.

Shipment of samples destined to the PNL 326 laboratory shall occur within 24 hours of the 222-S radiation screening. Trip blanks and field blanks are to accompany the waste samples to the laboratory. For specific information concerning sample and blank handling, custody, and transport refer to quality assurance/quality control requirements in Section 5.1.

## 4.5 Tank-Specific Analytical Procedures

### 4.5.1 Sampling, Isolation, and Analysis Scheme

A flowchart and narrative showing the sample collection, isolation, and analysis scheme is presented as Figure 2. All samples are to be prepared and analyzed in accordance with this scheme. Sample receipt, custody, preparation, and analysis shall be performed in accordance with approved procedures.

Following a time period for evaluation of the laboratory report by the Toxicology Review Panel (TRP), and if deemed necessary by the TRP, requirements for further quantification and speciation shall be conveyed through a Letter of Instruction by the Characterization Program and/or revision to this Tank Characterization Plan.

### 4.5.2 Analytical Methods

Sample material retrieved from the tank BY-103 vapor space and contained within the SUMMA® canisters shall be analyzed for total non-methane hydrocarbons following modified EPA procedures TO-12 and TO-14. The sorbent traps contain analyte-specific sorbent media and shall be analyzed for these specific analytes. The triple sorbent traps contain sorbent media designed to allow a broad range of organic species to be retained. Table 6 identifies the appropriate laboratory procedures used in each analysis.

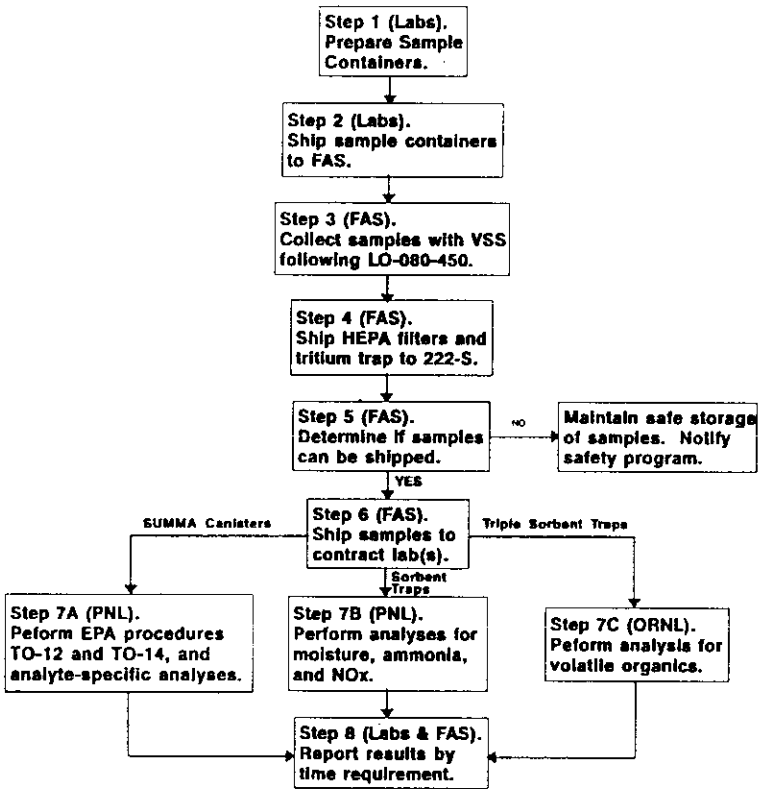
Any analyses prescribed by this document, but not performed, shall be identified and justification for non-performance written in the appropriate data report. If there are insufficient samples to perform all requested analyses, Tank Vapor Safety Resolution Program personnel shall be contacted.

**Figure 2. Test Plan Outline and Flowchart for Tank Vapor Space Characterization.**

- •Step 1 Prepare sample and blank containers at contract laboratories. Label containers using sample identification numbers and sampling data provided by Field Analytical Services.
- •Step 2 Ship containers to Field Analytical Services at least 4 days in advance of scheduled sampling event. Receipt and control of containers shall be guided by procedure PNL-TVP-07.
- •Step 3 If tank is safe with regard to flammability, set up vapor sampling system (VSS) and collect samples following procedure LO-080-450 and guidelines in Table 4.
- •Step 4 Perform radiological field survey of HEPA filters. Ship to the 222-S Laboratory the vapor sample containers for locker storage, and the HEPA filters and Tritium Trap for radiological survey.
- •Step 5 Using radiological survey report results, determine if samples are acceptable to ship offsite (see Section 4.4).
- •Step 6 If determined to be acceptable by offsite laboratory requirements and WHC-CM-2-14, ship samples and blanks following DOT requirements. If not acceptable to ship, maintain samples in storage and contact the J. W. Osborne of Vapor Issue Resolution Program for further direction.
- •Step 7 A. SUMMA® Canisters (PNL): Perform EPA-TO-12. Perform full scan EPA-TO-14. Perform analyte-specific analysis for the following: $H_2$, CO, $N_2O$, $CH_4$, $CO_2$.

  B. Sorbent Traps (PNL): Perform gravimetric analysis for moisture. Perform selective electrode analysis for $NH_3$ Analyze NO and $NO_2$ Traps.

  C. Triple Sorbent Traps (ORNL): Perform organic vapor analysis.
- •Step 8 Following the Section 8.0 reporting requirements, deliver a Format VI Report to the Vapor Issue Resolution Safety Program according to the contractual agreements .



## Table 6. BY-103 Sample Chemical, Physical, and Radiological Analytical Requirements

| PROJECT | BY-103 VAPOR |
|---|---|
| Plan Number | WHC-SD-WM-TP-231 |
| Tank | BY-103 |
| Program Contact | J. W. Osborne<br>J. L. Huckaby |
| TWRS Contact | B. C. Carpenter<br>C. S. Homi |
| Lab Project Coordinator | S. C. Goheen (PNL)<br>R. A. Jenkins (ORNL) |

**COMMENTS**

Type 3 vapor sampling system (VSS) using heated vapor probes.

**REPORT FORMATS**

| | |
|---|---|
| I | Early Notify |
| II | Process Control |
| III | Safety Screen |
| IV | Waste Management |
| V | RCRA Compliance |
| VI | Special |

**NUMBER OF SAMPLE/BLANK CONTAINERS PROCESSED**

| Organization | WHC | PNL | ORNL | TOTAL |
|---|---|---|---|---|
| SUMMA® Canister | | 6/2 | | 8[a] |
| Sorbent Trap System[b] | | 6/3 | | 9 |
| Triple Sorbent Trap | | | 4/2 | 6 |
| HEPA Filter | 4 | | | 4 |
| Tritium Trap | 1 | | | 1 |

**PRIMARY ANALYSES / QUALITY CONTROL[c] / CRITERIA**

| ANALYSIS METHOD | PRIMARY ANALYTE | PROCEDURE | LAB | SAMPLE PREP | SAMPLE CONTAINER | NO. OF SAMPLE | SURR SPIKE[d] | BLANK | ACTION LIMIT[e] | EXPECTED RANGE | PRECN | ACCURACY | REPORT FORMAT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| EPA TO-12 | TNMHC | PNL-TVP-004 | PNL | Direct | SUMMA® | 3 | none | 2 | N/A | 4-6 mg/m$^3$ | ±10% | 90-110% | VI |
| EPA TO-14 | Organic* Speciation | PNL-TVP-003<br>PNL-TVP-001 | PNL | Direct | SUMMA® | 3 | none | 2 | ≥ 4000 ppmv n-Butanol<br>50% IDLH for all others* | <100 ppbv | ±10% | 90-110% | I, VI |
| GC/TCD | $CO_2$<br>CO<br>$CH_4$<br>$H_2$<br>$N_2O$ | PNL-TVP-006 | PNL | Direct | SUMMA® | 3 | none | 2 | N/A<br>≥ 20% LFL<br>≥ 20% LFL<br>≥ 20% LFL<br>not available | not available<br>< 5 ppmv<br>not available<br>600-800 ppmv<br>700-900 ppmv | ±10%<br>±10%<br>±10%<br>±10%<br>±10% | 90-110% | VI<br>I, VI<br>I, VI<br>I, VI<br>I, VI |
| IC | NO<br>$NO_2$ | PNL-ALO-009 | PNL | $H_2O$ Extraction | Sorbent Trap | 4 | none | 1 | ≥ 150 ppmv<br>≥ 25 ppmv | not available<br>not available | ±10%<br>±10% | 90-110% | I, VI<br>I, VI |
| Gravimetric | $H_2O$ | PNL-ALO-009 | PNL | Direct | Sorbent Trap | 4 | none | 1 | N/A | not available | ±10% | 90-110% | VI |
| Selective Electrode | $NH_3$ | PNL-ALO-266 | PNL | $H_2O$ Extraction | Sorbent Trap | 4 | none | 1 | ≥ 250 ppmv | not available | ±10% | 90-110% | I, VI |
| GC/MS | Organics* | AC-MM-1-003153<br>AC-MM-1-003157 | ORNL | Thermal Desorption | Triple Sorbent Trap | 4 | all | 2[f] | ≥ 4000 ppmv n-Butanol<br>50% IDLH for all others* | < 100 ppbv | ±10% | 80-120% | I, VI |
| Total α<br>Total β<br>Total γ | Radon Daughters | LA-508-110<br>LA-508-111<br>LA-508-162 | WHC | Direct | HEPA Filter | 4 | N/A | N/A | ≥60 pCi/g α<br>≥60 pCi/g α<br>≥200pCi/g β/γ | <60 pCi/g α<br><60 pCi/g α<br><200 pCi/g β/γ | ±10%<br>±10%<br>±10% | 90-110% | I, II |
| Liq. Scin. | Tritium | LA-548-111 | WHC | Direct | Tritium Trap | 1 | N/A | N/A | N/A | not available | ±10% | N/A | II |
| GC/FID | Organics | LO-080-450 | FAS | Direct | On-line | N/A | N/A | N/A | N/A | N/A | N/A | N/A | II, VI |

N/A: Not Applicable

a Three canisters will be archived at PNL until arrangements can be made for transport and analytical work at the OGIST laboratory.

b System contains individual sorbent media sections for $NO_x$, $NH_3$, & $H_2O$.

c Multiple samples and blanks are taken.

d Samples are spiked with surrogates.

e Action required if any compound exceed 50% IDLH.

f Includes one trip and one field blank.

*Acetone, acetonitrile, benzene, 1,3- butadiene, butanal, n-butanol, n-dodecane, n-hexane, methane, propanenitrile, tributyl phosphate, n-tridecane. Other organic species detected at levels deemed sufficient by the laboratory scientist to be of potential toxicological concern shall be reported following Format I.

# 5.0 QUALITY ASSURANCE/QUALITY CONTROL

This Tank Characterization Plan and resultant laboratory analysis data has been approved by the WHC Environmental Safety, Health, and Quality Assurance (ESH&QA) Program provided the following conditions are met.

1) Each laboratory has a quality assurance program that meets the requirement of DOE order 5700.6C.

2) Each analysis and media preparation procedure given in Tables 3 and 6 are documented by the laboratory and available to ESH&QA.

3) Any modifications made to, or deviations from, the prescribed procedures are documented and justified in the deliverable report.

ESH&QA will qualify laboratories for continued use by the program after receipt of the Laboratory quality assurance plans, and an audit and corrective action phase.

## 5.1 Sampling Operations

The laboratory supplying the sample collection media shall initiate the chain of custody in accordance with the laboratory operating procedure LO-090-443, "Chain-of-Custody for RCRA and CERCLA Protocol Samples" using unique sample label and identification numbers provided by Field Analytical Services. Each sample identification number shall have the following format:

**SXXXX-WYY-LLL**, where:

| | | |
|---|---|---|
| **XXXX** | = | unique number assigned to the sampling event, |
| **W** | = | a letter code indicating the day of a multi-day sampling event, |
| **YY** | = | a 2-digit sample code found in Table 4, List of Sample and Activities, column one. |
| **LLL** | = | a special lab assigned code. |

Once the sample collection media has been received by FAS from the laboratory, it shall remain in the physical control of the custodian, locked in a secure area, or prepared for shipping with tamper evident tape. The sample collection media shall also remain in a controlled area under conditions specified by the sample collection media supplier.

Applicable operating procedures for the tank BY-103 vapor space sampling activities are contained in work package ES-94-1159. Vapor samples, trip blanks, and field blanks are to be collected in accordance with Tables 3 and 4 and laboratory operating procedure LO-080-450 "Collection of SUMMA® Canisters & Sorbent Tube Samples Using the Vapor Sampling System (VSS)" and shipped to the laboratory by Field Analytical Services in accordance with Hazardous Material Packaging and Shipping, WHC-CM-2-14.

All sampling activities shall be documented in controlled field logbooks maintained by sampling personnel (Sampling and Mobile Laboratories) and shall contain, but are not limited to:

1) identification of tank and riser number and photographs of the sample location in which the sampling is conducted,

2) if any anomalies are observed, corresponding sample identification numbers, flow rates, pressures, temperatures, and other operational parameters affecting the sample,
3) any conditions that the sampler may observe during the sampling event (i. e., odors, nearby machinery in operation, etc.),
4) names and titles of personnel involved in the field activity and their responsibilities,
5) instrument calibration dates.

Sampling and Mobile Laboratories is responsible for documenting any problems and procedural changes affecting the validity of the sample in a field notebook and shall enter this information in the comment section of the chain-of-custody form for addition to the data reports.

**5.2 Laboratory Operations**

Prepared and labeled sample collection containers, trip blanks, and field blanks are supplied by the performing laboratories to Field Analytical Services. The SUMMA® canisters and Sorbent Trap Systems are prepared and certified following the laboratory quality control procedures identified in Table 3. The laboratory supplying the sample collection media shall initiate the chain of custody in accordance with the laboratory operating procedure LO-090-443, "Chain-of-Custody for RCRA and CERCLA Protocol Samples" using sample label and identification numbers provided by Field Analytical Services.

The sample receipt and control procedures used in the Pacific Northwest Laboratory 326 Laboratory are reported by procedure PNL-TVP-07. Analyses performed at a laboratory shall be guided by a quality assurance program that meets the requirement of DOE order 5700.6C. The PNL 326 laboratory has an impact level II Laboratory Quality Assurance Plan (Barnes 1994).

Method specific quality control such as calibrations and blanks are also found in the analytical procedures. Sample quality control (duplicates, spikes, standards) are identified in Table 6. If no criteria are provided in Table 6, the performing laboratory shall perform to its quality assurance plan(s).

Due to the developmental work being done with the analysis procedures and potential sample differences (between tanks), changes in procedures may be needed. These changes must be documented in controlled notebooks referenced in the deliverable reports to ensure traceability.

## 6.0 ORGANIZATION

The organization and responsibility of key personnel involved in this tank BY-103 vapor sampling project are listed in Table 7.

**Table 7: Tank BY-103 Project Key Personnel List.**

| Individual(s) | Organization | Responsibility |
|---|---|---|
| S. C. Goheen | Pacific Northwest Laboratory | Project Manager for Vapor Sample Characterization |
| R. A. Jenkins | Oak Ridge National Laboratory | Project Manager for Vapor Sample Characterization |
| B. C. Carpenter C. S. Homi | TWRS Characterization Support | BY-103 Tank Characterization Plan Engineers |
| J. L. Huckaby | TWRS Tank Vapor Issue Resolution Program | Vapor Issue Resolution Engineer |
| H. Babad | TWRS Characterization Program | Tank Safety Screening Scientist |
| R. D. Mahon | Field Analytical Services | Sampling and Mobile Laboratories Vapor Sampling Program Lead |
| E. H. Neilsen | Waste Tank Safety Engineering | Vapor Sampling Cognizant Engineer |
| D. R. Carls | Industrial Hygiene and Safety Program | Industrial Hygiene Point of Contact if Action Limit is Exceeded (FAX 372-3522) |
| East Area Shift Operations Manager | Tank Farm Operations | East Tank Farm Point of Contact if Action Limit is Exceeded (373-2689) |

## 7.0 EXCEPTIONS, CLARIFICATIONS, AND ASSUMPTIONS

### 7.1 Exceptions to DQO Requirements

The determination of the flammability of tank vapor space gases will not be made *during* this sampling event. This determination is performed and reported *prior* to the sampling event by health physics personnel during periodic tank flammability testing. Once determined to be safe in regard to flammability, the tank is regarded as safe for a period of 6 months. During this period normal tank operations and sampling is permitted, following which a new flammability test may be performed.

## 7.2 Clarifications and Assumptions

Trip Blanks and Field Blanks

Trip Blanks are sampling devices prepared and handled in the same manner as samples, except that they are never opened in the field. Field Blanks are sampling devices prepared and handled in the same manner as the samples, but no tank samples are collected with them. Laboratories supplying blanks may opt to analyze only 1 trip blank unless it is determined to be contaminated, in which case all trip blanks are to be analyzed.

Sample Custodian

The sample custodian is the designated FAS cognizant scientist or assisting scientific technician, lead sampler, or laboratory scientist or technician who signs the *received by* block on the chain of custody. Transfer of custodianship occurs when the custodian signs the *relinquished by* block on the chain of custody and releases the sample(s) to the new custodian signator.

Physical Control

Physical control of a sample includes being in the sight of the custodian, in a room which shall signal an alarm when entered, or locked in a cabinet.

# 8.0 DELIVERABLES

The Pacific Northwest Laboratory, Oak Ridge National Laboratory, and Sampling and Mobile Laboratories VSS sampling and analyses of tank BY-103 vapors shall reported as Format VI (Section 8.3). All reports shall be submitted to J. W. Osborne of the Tank Vapor Safety Resolution Program. In addition, the analytical laboratories shall receive Format II reports from Sampling and Mobile Laboratories as described in Section 8.2. Table 6 identifies the primary analytes of concern and expected to be present in the vapor space of tank BY-103. Any analyte exceeding the notification limit prescribed in Table 6 shall be reported as Format I (Section 8.1). Other organic species detected at levels deemed sufficient by the laboratory scientist to be of potential toxicological concern shall also be reported following Format I. Other report recipients are identified in the following sections. Additional information regarding reporting formats is given in Schreiber (1994).

## 8.1 Format I Reporting

Table 6 contains the notification limits for specific analytes. Analytes that exceed notification limits defined in the DQO processes shall be reported by the Project Manager, delegate, or Health Physics Management by calling the East Area Shift Manager of Tank Farm Operations at (509) 373-2689 immediately. This verbal communication must be followed within 3 working days by written communication to J. W. Osborne of the Tank Vapor Issue Resolution Program, D. R. Carls in the Industrial Hygiene and Safety Program, and D. R. Bratzel of the Characterization Program, documenting the observation(s). A further review of the data, including quality control results and additional analyses for verification of the exceeded analyte, may be contracted between the performing laboratory and the contacts above.

## 8.2 Format II Reporting

Results of the 222-S Laboratory's radiological survey shall be reported by Sampling and Mobile Laboratories as Format II to the analytical laboratories listing the picocuries per sample (pCi/g of sample) for each sample submitted for analysis. This Format II report should also provide the sample collection sequence and

volumes, verification of trip and field blank use, and any anomalous sampling conditions to accompany, if possible, the shipment of samples. Alternatively, this sampling report may be transmitted by FAX to the analytical laboratories within 48 hours after the samples have been shipped.

### 8.3 Format VI Reporting

The final sampling report from Sampling and Mobile Laboratories shall be a WHC supporting document, with sponsor-limited release. It should include:

1) A description of sampling equipment used;
2) a description of sampling quality controls applied (e.g., leak and cleanliness tests of the sampling manifold, system temperature and pressure monitoring/alarms, instrument calibration details);
3) sampling event chronology and sample collection schedule (complete list of samples, by ID#, time collected, flow rates, etc.);
4) any industrial hygiene tank monitoring data collected before or during sampling event;
5) an evaluation of sources of sampling errors;
6) sample radiation screening results;
7) sample storage and shipment details; and
8) copies of all chain-of-custody forms.

Reports by the analytical laboratories shall be suitable for public distribution. To the extent applicable, the reports should include:

1) A summary of analytical results;
2) a description of sample device preparation (and manufacture if appropriate), citing procedures and logbooks used;
3) references providing traceability of sample device cleanliness;
4) a brief description of analytical methods, with procedures cited;
5) a brief explanation of how analytical systems control was demonstratably maintained;
6) a brief description of sample storage and shipment conditions, citing procedures and logbooks used;
7) a listing of analytes of quantitation (target analytes), with analytical method detection limit, range for which instrumentation is calibrated, number of calibration points used, and statistical data on linearity of calibration;
8) quantitative analytical results, expressed as dimensionless (ppmv or ppbv) concentration, and mass concentration ($\mu g/m^3$, mg/L, etc., calculated at 0 °C and 1 atm) of target analytes (identified by name and Chemical Abstract Service number) in each tank air sample;
9) tentative identification and semi-quantitative analytical results, expressed in both mass and dimensionless concentrations (if possible) of non-target organic analytes (identified by name and Chemical Abstract Service number) in each organic vapor sample;
10) a statistical summary (i.e., mean, standard deviation) for multiple analyses and/or multiple samples for all analytes (positively and tentatively identified compounds) in both mass and dimensionless concentrations (if possible);
11) a summary of all exceptional conditions, such as deviations from procedure or protocol, results obtained outside of instrument calibration range, sorbent trap breakthrough of analytes, or poor surrogate recoveries; and
12) chain-of-custody forms attached.

## 9.0 CHANGE CONTROL

Under certain circumstances, it may become necessary for the performing laboratory to make decisions concerning a sample without review of the data by the customer or the Characterization Program. These changes shall be brought to the attention of the project manager and the Characterization Program as quickly as possible and documented accordingly. Changes must be justified in their documentation. Changes may be documented through the use of internal change notices or analytical deviation reports for minor, low-impact changes. All significant changes (such as changes in scope) shall be documented by Characterization Support via an Engineering Change Notice to this Tank Characterization Plan. All changes shall also be clearly documented in the final data package.

Additional analysis of sample material from this vapor space characterization project at the request of the Characterization Program shall be performed according to a revision of this Tank Characterization Plan.

## 10.0 REFERENCES

Anderson, J. D., 1990, *A History of the 200 Area Tank Farms*, WHC-MR-0132, Westinghouse Hanford Company, Richland, Washington.

Barnes, B. O., 1994, *Quality Assurance Plan for TWRS Waste Tank Safety Program*, MCS-027 Rev. 4, Pacific Northwest Laboratory, Richland, Washington.

Bellus, T. H., 1993, *Configuration of Hewlett Packard (HP) 5890 Series II Gas Chromatograph (GC) for DML1*, (internal memo 12240-SAA93-039 to L. L. Lockrem, July 10), Westinghouse Hanford Company, Richland, Washington.

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Keller, K. K., 1994, *Quality Assurance Project Plan for Tank Vapor Characterization*, WHC-SD-WM-QAPP-013, Rev.2, Westinghouse Hanford Company, Richland, Washington.

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Osborne, J. W., 1994b, *Letter of Instruction to Sandia National Laboratory and Oregon Graduate Institute of Science and Technology for Analysis of SUMMA Canister Samples Collected from Tanks 241-BY-103, 241-BY-104, 241-BY-105, 241-BY-106, 241-BY-107, 241-BY-108, and 241-BY-111*, (letter 9452039 to Dr. W. Einfeld, March 23), Westinghouse Hanford Company, Richland, Washington.

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Schreiber, R. D., 1994, *Revised Interim Tank Characterization Plan Guidance*,(letter 7E720-94-121 to C. S. Haller, May 13), Westinghouse Hanford Company, Richland, Washington.

Whelan, T. E., 1994, *TWRS Characterization Program Quality Assurance Program Plan*, WHC-SD-WM-QAPP-025, Westinghouse Hanford Company, Richland, Washington.

# DISTRIBUTION SHEET

| To | From | Page 1 of 1 |
|---|---|---|
| Distribution | Characterization Support | Date 10-21-94 |
| Project Title/Work Order | | EDT No. 600675 |
| Tank 241-BY-103 Tank Characterization Plan (WHC-SD-WM-TP-231) | | ECN No. |

| Name | MSIN | Text With All Attach. | Text Only | Attach. / Appendix Only | EDT/ECN Only |
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| R. D. Schreiber (10) | R2-12 | X | | | |
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*(See instructions on reverse side. Use plain bond paper if additional space is needed for explanations.)*

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### A. Product/Report Data

1. (Award) Contract No. DE-AC06-87RL10930

2. Title TANK 241-BY-103 TANK CHARACTERIZATION PLAN

3. Product/Report Description

[X] a. Report *(Complete all that apply)*

(1) [X] Print [ ] Nonprint *(specify)* _____

(2) [ ] Quarterly [ ] Semiannual [ ] Annual [X] Final
[ ] Topical [ ] Phase I [ ] Phase II
[ ] Other *(specify)* _____

Dates covered _____ thru _____

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| [ ] | [X] | Is any new equipment, process, or material disclosed? |
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### C. Contact *(Person knowledgeable of content)*

Name B.C. CARPENTER
Phone 509-372-2349
Position AUTHOR
Organization WESTINGHOUSE HANFORD COMPANY

## PART II *(DOE/DOE Contractors complete/or as instructed by DOE contracting officer)*

### A. DOE Identifiers

1. Product/Report Nos. WHC-SD-WM-TP-231, REV.0

2. Funding Office(s) *(NOTE: Essential data)* EM

### B. Copies for Transmittal to AD-21 (OSTI)

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[ ] Has been submitted for DOE patent clearance
[X] DOE patent clearance has been granted

B. Released by
*(Name)* KARA BROZ
*(Signature)* Kara L Broz
*(Phone)* 509-373-3151
*(Date)* 11-14-94

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| Applied Technology-Export Controlled Information or International Program | [ ] | | | [ ] |
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| Other | [✓] | IRA - KM Broz | Kathleen Broz 10/21/94 | [ ] |

6. Applied Technology Material Referenced: [X] No [ ] Yes

7. Release Level: [X] Public [ ] Limited Distribution

8. Author/Requestor: B. C. CARPENTER (Print and Sign) Brad Carpenter 10/20/94 Date

9. Responsible Manager: C. S. HALLER (Print and Sign) R.D. Schreiber 10/20/94 Date

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A-6001-401 (07/94)

*10. LEGENDS/NOTICES/MARKINGS* (Required by WHC-CM-3-4 or Reviewer). Reviewer indicates applicable markings to be affixed or removed.

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| Availability - OSTI | ☐ | ☐ | | Patent Status | ☐ | ☐ | |
| Availability - ESTSC | ☐ | ☐ | | Predecisional Information | ☐ | ☐ | |
| Availability - NTIS | ☐ | ☐ | | Programmatic Notice | ☐ | ☐ | |
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*12. ADDITIONAL INFORMATION/COMMENTS:*